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13. ABSTRACT (Maximum 200 words)

The structure and dynamics of supercritical mixtures were studied by molecular dynamics and integral equation calculations. Integral equation calculations were performed on the systems naphthalene in carbon dioxide (non-volatile solute; attractive mixture); and neon in xenon (volatile solute; repulsive mixture), at high dilution and at supercritical temperatures. The attractive system exhibited significant short-ranged solvent enrichment around the solute at sub-critical densities. Molecular dynamics calculations were performed for the system benzene in carbon dioxide, from 50% to twice the critical density, at supercritical temperatures. Enhancements in local density of carbon dioxide around benzene were more pronounced at sub-critical density. Neither local density augmentation nor proximity to the critical point affected the solute's translational and rotational diffusivities. These quantities varied smoothly with bulk density across the range of conditions investigated. The main conclusion from this work is that local-bulk asymmetries are most pronounced at sub-critical densities, and that the dynamics of solute molecules at high dilution are unaffected by the proximity to the solvent's critical point.

14. SUBJECT TERMS

Molecular dynamics simulation; solvation and dynamics in supercritical mixtures; integral equation calculations.

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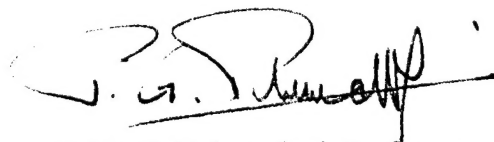
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COMPUTER SIMULATIONS OF MOLECULAR INTERACTIONS IN SUPERCRITICAL SOLVENTS

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1. Objective

The objective of this project was to investigate theoretically the microscopic structure and dynamical behavior of dilute supercritical mixtures. This was accomplished using two methods: integral equation calculations and molecular dynamics simulations. The former provides information on the spatial distribution of molecular species; the latter also provides information on dynamics.

2. Main Findings

2.1 Integral Equation Calculations

Two highly dilute binary supercritical systems were studied: one attractive and one repulsive. The spherically-symmetric Lennard-Jones potential was used in both cases. According to the classification introduced by Debenedetti and co-workers (Petsche and Debenedetti, 1991), attractive mixtures consist of a large, non-volatile solute dissolved in a volatile supercritical solvent; the solute's characteristic interaction energy is correspondingly larger than the solvent's. Repulsive behavior occurs when the solvent is larger than the solute and has a correspondingly higher characteristic interaction energy. In attractive mixtures, there is long-range solvent enrichment around solute molecules in the vicinity of the solvent's critical point; solubility is enhanced with respect to ideal-gas behavior at the same temperature and pressure; and the solute's partial molar volume and enthalpy are large and negative, diverging to $-\infty$ at the solvent's critical point in the limit of infinite dilution. In a repulsive mixture, there is long-range solvent depletion around solute molecules in the neighborhood of the critical point, and the solute's partial molar volume and enthalpy are large and positive, diverging to $+\infty$ at the solvent's critical point in the limit of infinite dilution. Potential parameters for both mixtures are listed in tables I and II.

Table I. Lennard-Jones Parameters for Naphthalene in CO_2

Naphthalene in CO_2	ij	σ_{ij} (Å)	σ_{ij}/σ_{22}	ε_{ij}/k (K)	$\varepsilon_{ij}/\varepsilon_{22}$
solute-solute	11	6.199	1.634	554.4	2.458
solvent-solvent	22	3.794	1.000	225.5	1.000
solute-solvent	12	4.996	1.317	353.4	1.5677

Table II. Lennard-Jones Parameters for Neon in Xenon

Neon in Xenon	ij	σ_{ij} (Å)	σ_{ij}/σ_{22}	ε_{ij}/k (K)	$\varepsilon_{ij}/\varepsilon_{22}$
solute-solute	11	2.820	0.697	32.8	0.142
solvent-solvent	22	4.047	1.000	231.0	1.000
solute-solvent	12	3.433	0.848	87.0	0.377

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The mixtures listed in Tables I and II have been called naphthalene (solute) in carbon dioxide (solvent) (Cochran and Lee, 1989) and neon (solute) in xenon (solvent) (Petsche and Debenedetti, 1989). We use this terminology, although it should be understood that except for yielding reasonable estimates for pure-component critical temperatures and densities with the parameters listed in Tables I and II, the Lennard-Jones potential is a rudimentary representation of the actual interaction potentials.

The most important findings that resulted from this work were:

(a) Large enhancements in the calculated local density of solute molecules around a central solute molecule. Local densities roughly an order of magnitude in excess of the bulk density were found. This is illustrated in Figure 1.

(b) Local-bulk asymmetry is most pronounced at sub-critical densities. The maximum enhancement in the solute-solute distribution function shown in Figure 1 occurs at a reduced density of 0.58. The fact that such pronounced local-bulk asymmetries are more important at sub-critical densities had not been previously understood.

(c) The solute's chemical potential is determined by short-ranged solvation interactions. This is illustrated in Figure 2, which shows the cutoff distance (beyond which the mixture is assumed to be homogeneous) needed to obtain specified percentages of the asymptotic value of the solute's fugacity coefficient.

(d) Large depletions in the distribution of solvent molecules around the solute exist in repulsive mixtures. This is illustrated in Figure 3.

Taken together, (a) and (b) imply that solvation and local-bulk asymmetry are unrelated to proximity to critical points. These short-ranged effects are a consequence of differences in size and characteristic interaction energy between the solute and the solvent.

2.2 Molecular Dynamics Simulations

The objective of this study was to understand the mechanisms of solvation in supercritical solvents, and in particular to understand in what ways the translational and rotational

motion of solutes is affected by high local solvent densities. The system benzene (solute) - carbon dioxide (supercritical solvent) was investigated. Both molecules were modeled as rigid polyatomics interacting via multi-site Lennard-Jones potentials. In addition, interactions between carbon dioxide molecules included a point quadrupole moment. Site parameters are listed in Table III.

Table III. Site Potential Parameters for Benzene-Carbon Dioxide Simulations[a]

Molecule		ε/k (K)	σ (Å)
Carbon Dioxide			
	C-C	29	2.785
	O-O	83.1	3.014
Benzene			
	CH-CH	95.05	3.350

(a) Lorentz-Berthelot used for unlike pairs. CO distance = 1.16 Å; CH-CH distance = 1.765 Å

Simulations were done at two reduced temperatures (T/T_c = 1.05, 1.1) and five reduced densities (ρ/ρ_c = 0.5, 0.75, 1, 1.5, 2). In both cases, the critical parameters are the solvent's.

The main results of this work were:

(a) The distribution of solvent molecules around benzene is highly asymmetric. Benzene is preferentially solvated in the polar position, where the solvent density can be as high as seven times its bulk value. This is shown in Figure 4. Note that the difference between local and bulk conditions is more pronounced at the lowest density investigated. No unusual solvation effects are seen at the critical density.

(b) Benzene's translational diffusion in supercritical carbon dioxide scales inversely with bulk density, and is unaffected by proximity to the critical point. This is shown in Figure 5.

(c) The rotational motion of benzene is remarkably insensitive to bulk density over the range of densities explored. No transport anomalies were found near the solvent's critical point.

(d) The diffusive exchange of solvation shell molecules is described by a single exponential, with a time constant that increases monotonically with increasing density. This time constant ranges from 3 psec at 50% of the critical density to 7 psec at twice the critical density. This is shown in Figure 6.
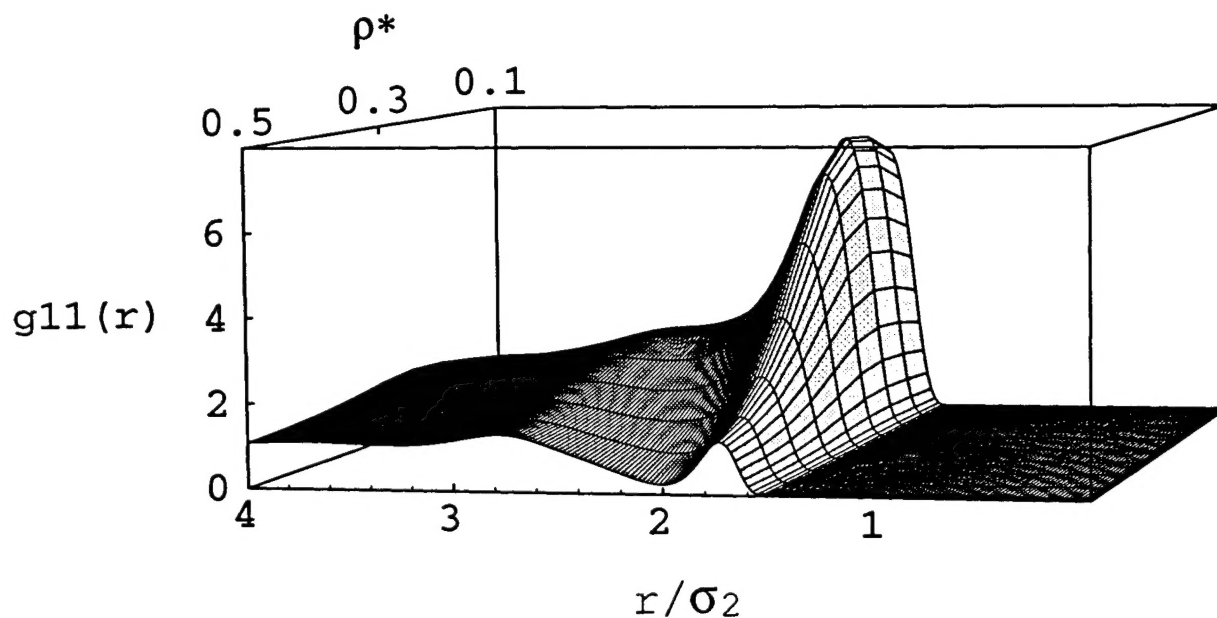
Figure 1: Integral equation calculation of the density dependence of the solute-solute pair correlation function for the naphthalene-carbon dioxide system. The vertical axis is the ratio of local to bulk concentration of naphthalene molecules around a central naphthalene molecule. The transverse axis is the distance from the central naphthalene molecule, in units of the Lennard-Jones diameter of carbon dioxide (Table I). ρ^* is the number density (molecules per unit volume), in units of the cube of the Lennard-Jones diameter of carbon dioxide. The critical density of the pure solvent is at $\rho^* = 0.31$. The temperature is 7% above the solvent's critical point, and the solute mole fraction is 10^{-9}. Note the large first peak, especially at sub-critical densities. (Tom and Debenedetti, 1993).
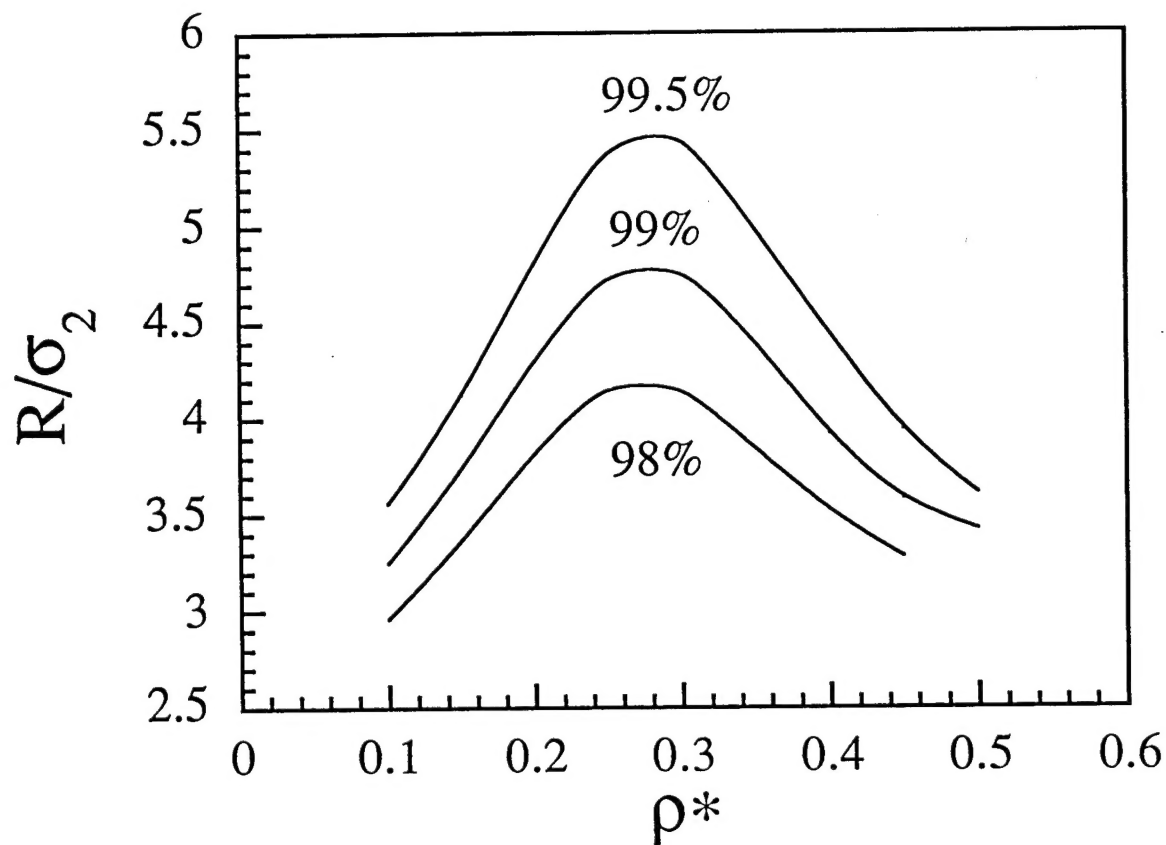
Figure 2: Integral equation calculation of the cutoff distance needed to obtain the specified percentages of the asymptotic value of the solute's fugacity coefficient. System naphthalene (solute)-carbon dioxide (solvent). The cutoff (vertical axis) is in units of carbon dioxide's Lennard-Jones diameter (Table I). Temperature and mole fraction as in Figure 1. Density units as in Figure 1. The cutoff distance calculated here is the solvation region that defines the solute's chemical potential. Thus, the calculations show that solubility is determined by the local environment within 11 to 20 Å around a central naphthalene molecule. (Tom and Debenedetti, 1993).
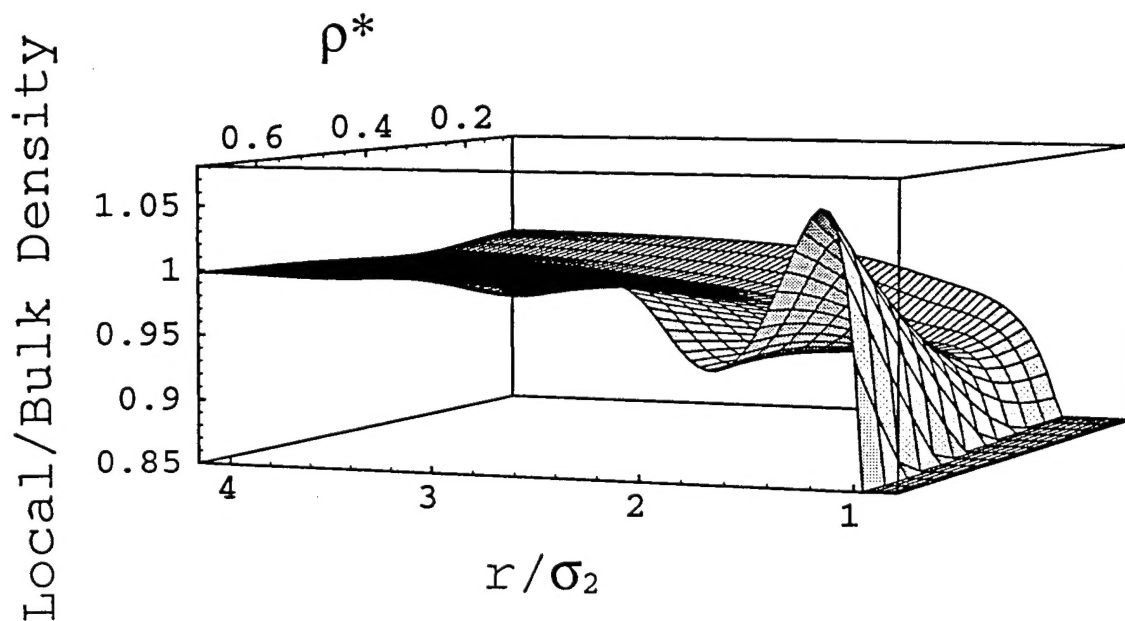
ρ*

Local/Bulk Density

0.6   0.4   0.2

1.05
1
0.95
0.9
0.85

4   3   2   1

r/σ₂

Figure 3: Integral equation calculation of the density dependence of the ratio of local-to-bulk density of supercritical xenon atoms around a central neon atom. The density is averaged over a sphere of specified radius, expressed in units of the Lennard-Jones diameter of xenon (Table II). ρ^* is the number density (molecules per unit volume), in units of the cube of the Lennard-Jones diameter of xenon. The critical density of the pure solvent is at $\rho^* = 0.31$. The temperature is 7% above the solvent's critical point, and the solute mole fraction is 10^{-9}. Note the large depletion region where the local density is smaller than the bulk. This is due to the mixture's repulsive behavior. (Tom and Debenedetti, 1993).
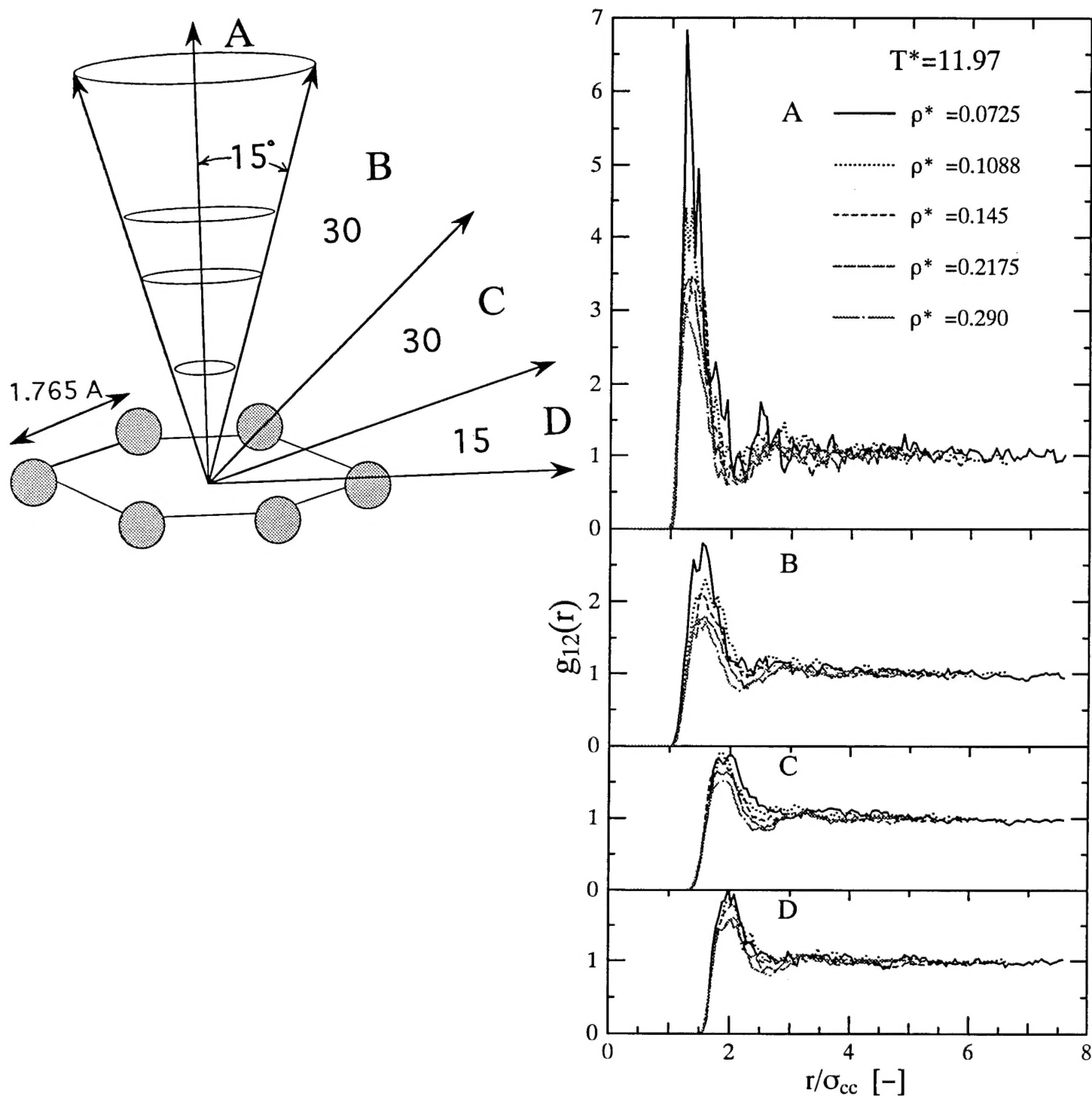
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Figure 4: Sector-dependent radial distribution function of supercritical carbon dioxide around benzene. g is the ratio of local to bulk density. Also shown is the geometry for the definition of sectors. $T^* = kT/\varepsilon_{cc}$; $\rho^* = \rho\sigma^3_{cc}$ (see Table III for ε_{cc} and σ_{cc} values). T (K) = 29T^*; ρ (mol/liter) = 76.87 ρ^*. For the potential parameters used in this study, T_c = 330.6 K (T^* = 11.4); ρ_c = 11.15 mol/liter (ρ^* = 0.145). The two salient features are the preferential solvation by carbon dioxide in the polar region, and the fact that the most pronounced enhancements in local solvent density occur at sub-critical densities. Molecular dynamics simulation. (Inomata et al., 1996).
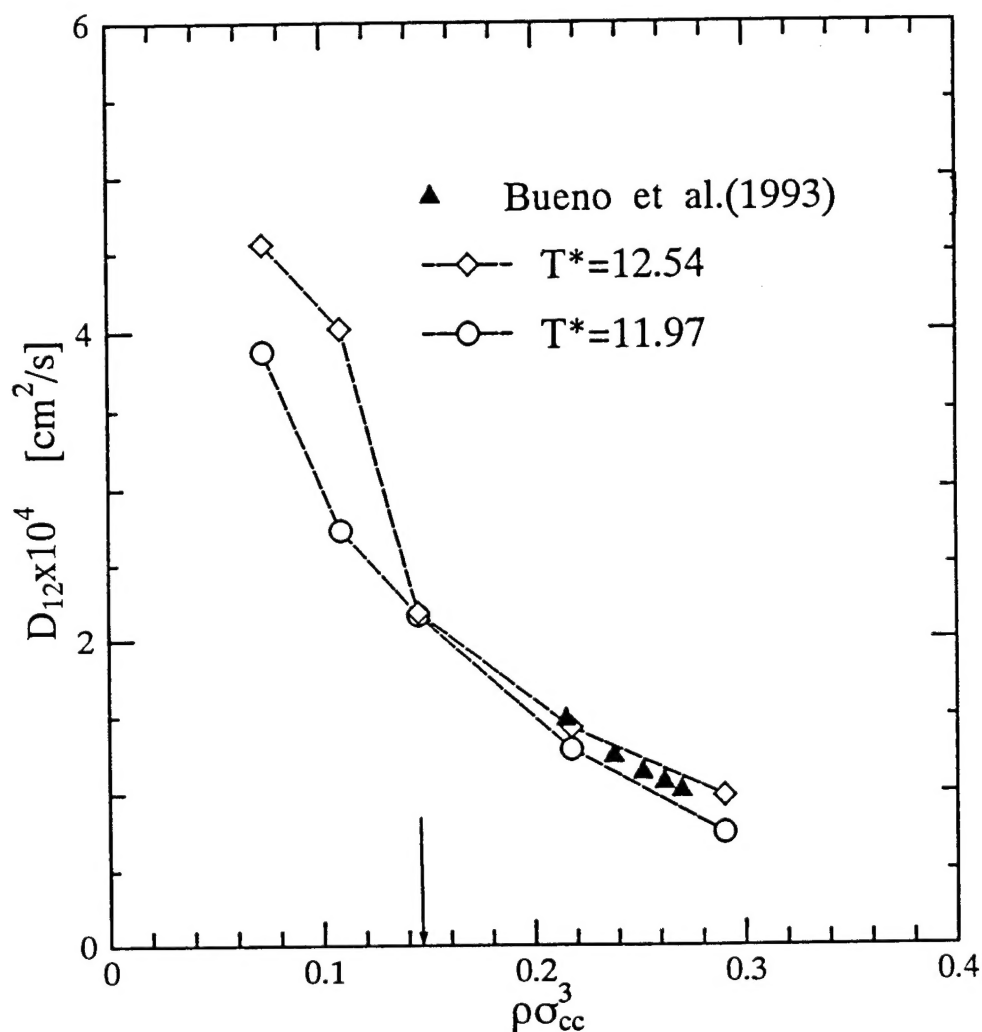
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Figure 5: Translational diffusion coefficient of benzene in carbon dioxide at two supercritical temperatures. Vertical arrow indicates carbon dioxide's critical density. Experimental data are from Bueno et al., *J.Chem.Eng.Data, 38*, 344 (1993). $T^* = kT/\varepsilon_{cc}$; $\rho^* = \rho\sigma^3_{cc}$ (see Table III for ε_{cc} and σ_{cc} values). T (K) = $29T^*$; ρ (mol/liter) = 76.87 ρ^*. For the potential parameters used in this study, T_c = 330.6 K ($T^* = 11.4$); ρ_c = 11.15 mol/liter ($\rho^* = 0.145$). Note the smooth variation of the translational diffusivity in the critical region. Molecular dynamics simulation. (Inomata et al., 1996).
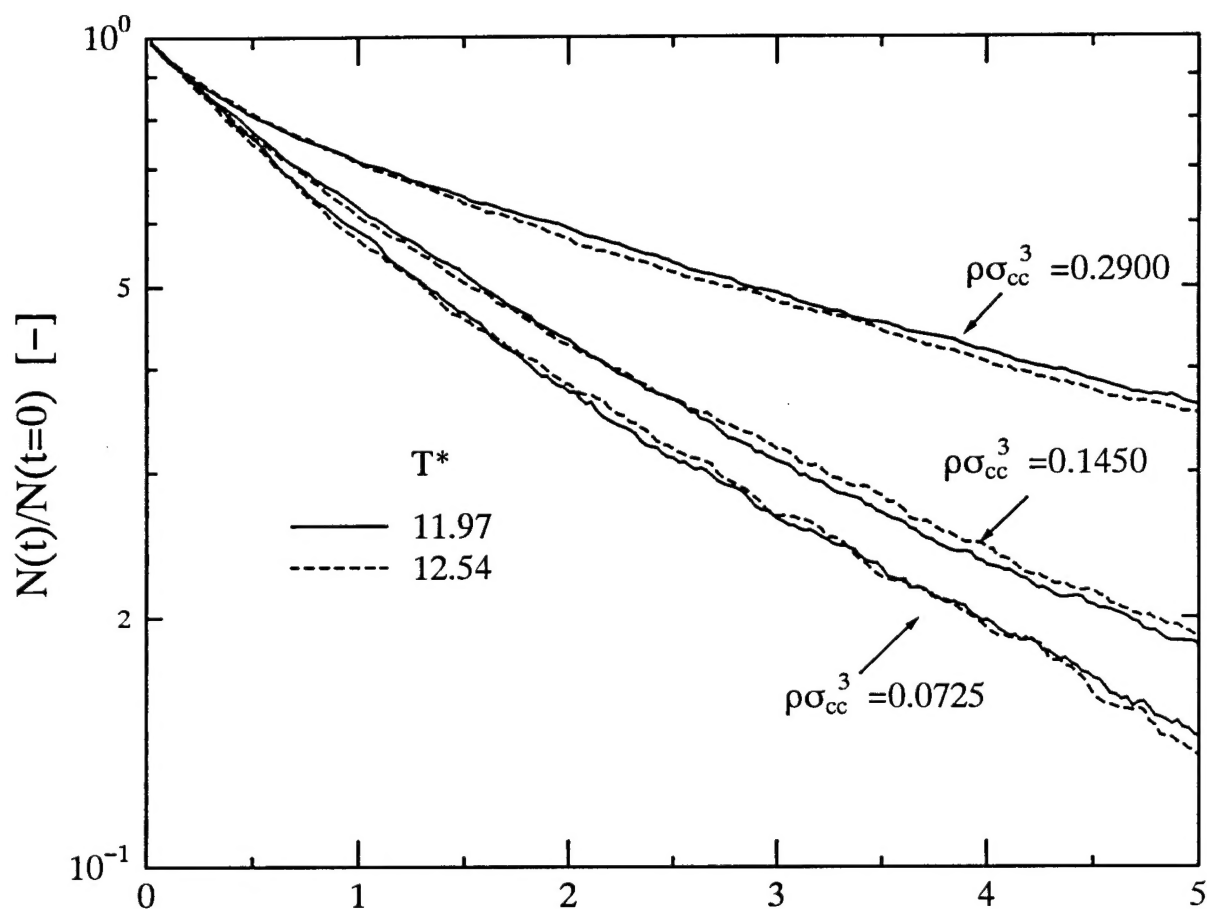
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Figure 6: Decay of the fraction of tagged carbon dioxide molecules within a sphere of radius 6.7 Å centered at benzene's center of mass that remain in the sphere at time t. $T^* = kT/\varepsilon_{cc}$; $\rho^* = \rho\sigma^3_{cc}$ (see Table III for ε_{cc} and σ_{cc} values). T (K) $= 29T^*$; ρ (mol/liter) $= 76.87 \rho^*$. For the potential parameters used in this study, $T_c = 330.6$ K ($T^* = 11.4$); $\rho_c = 11.15$ mol/liter ($\rho^* = 0.145$). The decay is described by a single exponential. Note the slowing down of the decay rate upon increasing the density.

3. Publications Describing AFOSR-Sponsored Research, 11/1/92 - 2/1/96

J.W. Tom and P.G. Debenedetti, "Integral Equation Study of Microstructure and Solvation in model Attractive and Repulsive Supercritical Mixtures", **Ind. Eng. Chem. Res., 32**, 2118 (1993).

S.-D. Yeo, P.G. Debenedetti, M. Radosz, and H.-W. Schmidt, "Supercritical Anti-Solvent (SAS) Process for Substituted Para-Linked Aromatic Polyamides: Phase Equilibrium and Morphology Study", **Macromolecules, 26**, 6207 (1993).

J.W. Tom, P.G. Debenedetti, and R. Jérome, "Precipitation of Poly(L-lactic acid) and Composite Poly(L-lactic acid)-Pyrene Particles by Rapid Expansion of Supercritical Fluids", **J. Supercrit. Fluids, 7**, 9 (1994).

P.G. Debenedetti, "Supercritical Fluids as Particle Formation Media", in *Supercritical Fluids. Fundamentals for Applications.* E. Kiran and J.M.H. Levelt-Sengers, eds. **NATO ASI, Ser. E, 273**, 719 (1994).

P.G. Debenedetti, "Solute-Solute Interactions: Theory and Simulation", in *Supercritical Fluids. Fundamentals for Applications.* E. Kiran and J.M.H. Levelt-Sengers, eds. **NATO ASI, Ser. E, 273**, 439 (1994).

S.-D. Yeo, P.G. Debenedetti, S. Patro, and T.M. Przybycien, "Secondary Structure Characterization of Microparticulate Insulin Powders", **J. Pharm. Sci., 83**, 1651 (1994).

S.-D. Yeo, P.G. Debenedetti, M. Radosz, H.-W. Schmidt, and R. Giesa, "Supercritical Anti-Solvent (SAS) Process for a Series of Substituted Para-Linked Aromatic Polyamides", **Macromolecules, 28**, 1316 (1995).

H. Inomata, P.G. Debenedetti, and S. Saito, "Molecular Dynamics Simulation of Infinitely Dilute Solutions of Benzene in Supercritical CO2", **Fluid Phase Equil.**, in press (1966).

M. A. Winters, B.L. Knutson, P.G. Debenedetti, H.G. Sparks, T.M. Przybycien, C.L. Stevenson, and S.J. Prestrelski, "Precipitation of Proteins in Supercritical Carbon Dioxide", **J.Pharm.Sci.**, in press (1996).

4. Technical Presentations on AFOSR-Sponsored Research, 11/1/92 - 2/1/96

"Solvation, Nucleation, and Particle Formation in Supercritical Fluids." Fuel Science Program, Department of Materials Science, Pennsylvania State University, University Park, April 16, 1993.

"Supercritical Fluids: Fundamentals and Applications." Sixth International Congress on Engineering and Food, Chiba, Japan, May 26, 1993.

"Solute-Solute Interactions in Supercritical Solutions: a Molecular Dynamics Investigation." Symposium on Scientific Research on Supercritical Fluids, University of Tokyo, Japan, May 31, 1993.

"Solute-Solute Interactions: Theory and Simulations." NATO Advanced Study Institute on Supercritical Fluids: Fundamentals for Application, Kemer, Turkey, July 22, 1993.

"Molecular Dynamics Study of Solute-Solute Interactions in Dilute Supercritical Mixtures." AIChE Annual Meeting, St. Louis, MO, November 10, 1993.

"Computer Simulation of Molecular Interactions in Supercritical Solvents." Advanced Fuels Workshop, Wright-Patterson Air Force Base, Ohio, February 7, 1994.

"Supercritical Fluids as Particle Formation Media." Department of Chemical Engineering, Yale University, March 28, 1994.

"Supercritical Fluids as Particle Formation Media." AIChE Central Jersey Section, Princeton University, May 19, 1994.

"Supercritical Fluids as Particle Formation Media." Robert L. Mitchell Technical Center, Hoechst Celanese Corporation, Summit, New Jersey, July 14, 1994.

"Supercritical Fluids as Particle Formation Media." 3rd International Symposium on Supercritical Fluids, Strasbourg, France, October 17, 1994.

"Supercritical Fluids as Particle Formation Media." Alza Corporation, Palo Alto, California, December 9, 1994.

"Simulation of Structure and Dynamics at Supercritical Conditions." Wright-Patterson Air Force Base, Dayton, Ohio, March 10, 1995.

"Materials Processing with Supercritical Fluids." Merck research Laboratories, Rahway, New Jersey, May 1, 1995.

"Supercritical Fluids." Four-lecture course. Astra-Hässle, Mölndal, Sweden, May 22-23, 1995.

"Computer Simulation of Molecular Interactions in Supercritical Solvents." AFOSR Workshop on Supercritical Fuels, Ann Arbor, Michigan, June 15, 1995.

"Materials Processing with Supercritical Fluids". Department of Chemistry and Biochemistry, University of Southern Illinois, Carbondale, Illinois, September 8, 1995.

"Materials Processing with Supercritical Fluids". Invited tutorial. American Association for Aerosol Research, 14th annual meeting. Pittsburgh, Pennsylvania, October 9, 1995.

5. Personnel

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